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(71) Applicant (for all designated States except US): **DOW CORNING IBERICA S.A.** [ES/ES]; Avda Diagonal, 613:5, E-08028 Barcelona (ES).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **RAMON LOPEZ, Anton** [ES/ES]; C/Ripoll, 34, Urbanizacio Can Duran, Palau-Solita I Plegamans, E-08184 Barcelona (ES). **UBALDO, Colombo** [IT/IT]; Via Delle Orchidee, 2, I-20020 Vanzaghello (IT).

(74) Agents: **DONLAN, Andrew, M.** et al.; Dow Corning Limited, Intellectual Property Department, Cardif Road, Barry CF63 2YL (GB).

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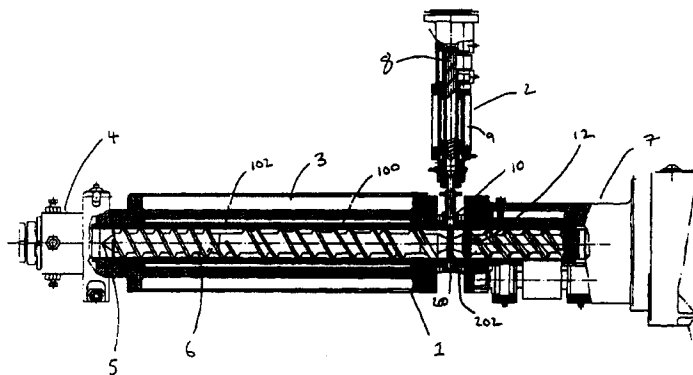
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[Continued on next page]

(54) Title: EXTRUDER



(57) Abstract: The invention relates to a single screw extruder having a means for the introduction of additives and to a method of introducing additives into a silicone rubber composition in the aforementioned extruder. A single screw extruder (1) comprising an elongate barrel (100) having an inlet (7) for introducing a polymer into the extruder and an outlet (5) for discharging extruded polymer from the barrel (100), a rotatable screw (6) axially disposed within the barrel (100) for advancing polymer in the extruder from the inlet (7) to the outlet (5), one or more additive introduction means (2) for introducing one or more additives at one or more predefined positions along the barrel (100) of the single screw extruder (1) between the inlet (7) and the outlet (5). Immediately upstream of the or each additive introduction means (2) there is provided, on or around the screw (6), a plug (12) having a plurality of apertures (20, 20a) which is adapted such that, in use, the only way for polymer or polymer/additive mixture to move downstream of the plug (12) is by passing through the apertures and that, having passed through an aperture, the polymer or polymer/additive mixture is subjected to a reduction in pressure and is simultaneously mixed with an additive from the one or more additive introduction means (2), prior to transportation of the resulting polymer additive mixture to the outlet (5). The extruder is typically used for the addition of additives such as cross-linkers and/or coloured pigments into high consistency silicone rubbers.

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## EXTRUDER AND METHOD FOR CONTINUOUSLY MIXING SILICONE RUBBER

[0001] The present invention relates to a single screw extruder and in particular to a single screw extruder having a means for the introduction of additives and to a method of  
5 introducing additives into a silicone rubber composition in the aforementioned extruder.

[0002] Extruders having side arm extruders for the introduction of additives are well known for organic rubbers and plastics. US 5749649 describes an extrusion arrangement for the compounding and mixing of a plurality of substances in a single screw extruder having  
10 satellite extruders for the high pressure introduction of components such as colorants and extenders which may not otherwise survive the mixing process because of otherwise damaging temperatures, pressures or mixing characteristics.

[0003] US 4657499 describes a screw extruder for introducing additive fluids into a screw type extrusion apparatus. The additive fluids which are introduced by means of an  
15 injection port are particularly used in combination with thermoplastic materials such as cellulose acetate, polyvinyl chloride (PVC), nylon, polyethylene and acrylic resins. There is no indication that such an extruder is intended for silicone rubber. Other systems for the introduction of additives into organic feedstock being transported along extruders include US  
20 4289408 and GB 2059864.

[0004] It will be clear to a man skilled in the art that the above prior art relates to extruders for organic polymers/rubbers as opposed to silicone rubber extruders because there are significant processing differences between the two. For the purpose of this invention it is  
25 to be understood that an organic rubber has a substantially carbon – carbon polymer backbone and a silicone rubber has a substantially siloxane (-Si-O-Si-) polymer backbone. Reasons for the differences in extruder processing of organic rubbers and silicone rubbers include, for example, the fact that organic rubber has a significantly lower adhesion to the inner wall of an extruder barrel than silicone rubber and as such it is necessary to apply shear in the extruder  
30 to heat organic rubber for processing. Typical organic rubber extruders require an extruder barrel having a screw with a Length: Diameter (L:D) ratio of between 15:1 to 22:1 with a screw geometry designed to cause shearing of the organic rubber. Screws for organic rubber extruders may be provided with double flights having different flight pitches to force the

rubber to flow over the flights. Alternatively pin extruders may be utilised which comprise pins in the barrel used to increase shear and output preventing organic rubber from progressing along the inner walls of the extruder barrel.

5     **[0005]**         In comparison the viscosity of silicone rubber changes only slightly within the temperature range of 20-60°C (unlike organic rubbers). Silicone rubbers do not require any heating effect or increase in shear. Indeed preferably the melt temperature of silicone rubber is kept as low as possible during the period of time spent in an extruder barrel in order to avoid partial vulcanisation (scorch). Adhesion of silicone rubber to the internal wall of an  
10     extruder barrel (wall adhesion) is significantly greater than with organic rubber equivalents and as such heat absorption and temperature increases occur due to the shearing forces on the silicone rubber between the screw and the inner wall of the extruder barrel. Typically silicone rubber extruders have a barrel cooling system. Silicone rubber extruders therefore require shorter screw lengths of 8 to 15 diameters (D) and utilise internal cooling systems for  
15     extruding silicone rubber.

**[0006]**         In some instances it may be possible to process silicone rubber through extruders designed for organic rubber but due to their high shear design and, in most cases, the lack of an appropriate cooling system, there are significant limitations in particular the  
20     fact that very low screw speeds will be required for processing silicone rubber to avoid scorching problems in the extruder barrel. Furthermore, Silicone rubber extruders are much more difficult to clean than organic rubber extruders and extruded silicone rubbers require better compression than organic rubbers.

25     **[0007]**         Conventionally it is known to the skilled man in the art of silicone rubber extruders that single extruders are generally used only for transportational purposes as they provide poor mixing. Multiple screw systems (typically twin screw) are generally used where mixing is required for silicone rubber.

30     **[0008]**         The applicant has now identified a single screw extruder which may be used to thoroughly mix an additive introduced through a side arm unit into a polymer to produce a homogeneous polymer/additive mixture prior to reaching the head of the extruder.

[0009] In accordance with the present invention there is provided a single screw extruder comprising

- a) an elongate barrel having an inlet for introducing a polymer into the extruder and an outlet for discharging extruded polymer from the barrel
- 5 b) a rotatable screw axially disposed within the barrel for advancing polymer in the extruder from the inlet to the outlet
- c) one or more additive introduction means for introducing at least one additive at one or more predefined positions along the barrel of the single screw extruder between the inlet and the outlet,

10 wherein

immediately upstream of the or each additive introduction means there is provided, on or around the screw, a plug having a plurality of apertures, said plug being adapted such that, in use, the only way for polymer or polymer/additive mixture to move downstream of the plug is by passing  
15 through the apertures and that, having passed through the apertures, the polymer or polymer/additive mixture is subjected to a reduction in pressure and is simultaneously mixed, with an additive from the one or more additive introduction means, in a mixing zone section, prior to transportation of the resulting polymer/additive mixture to the outlet.

20

[0010] Preferably the single screw extruder is a silicone rubber extruder.

[0011] The extruder barrel is preferably substantially cylindrical in shape and may be of any appropriate length. The screw may be of any appropriate diameter but preferably has a  
25 diameter of from 30 to 150mm, more preferably from 60 to 120mm and has a length to diameter (L/D) ratio of from 8:1 to 15:1, preferably about 10:1 to 15:1. The rotational speed of the screw may have a maximum of 100 revolutions per minute (r.p.m.) but is preferably between 3 to 40 r.p.m.

30 [0012] In use, polymer is preferably fed through the elongate barrel inlet by way of a feeding body having a chamber for optional thermal conditioning of the polymer prior to introduction onto the extruder and a feeding chamber made for example from case-hardened and/or tempered steel. A feed roller may be utilised to assist in the introduction of the

polymer into the extruder. The feed roller may be made of any appropriate material but is preferably made from case-hardened and/or tempered steel and comprises a rotary joint for optional heating/cooling. The feed roller may be provided with a scraper and/or an adjustable blade and polymer may be introduced onto the feed roller by any appropriate means such as a feed hopper.

[0013] In use polymer/additive mixture exiting the barrel will usually pass directly into an extrusion head which may be adapted to form any appropriately shaped silicone rubber product(s). Examples of products suitable to be made using the extruder of the present invention include hoses and coated wires. Subsequent to passing through the extrusion head the resulting extruded product may be cured in an appropriate oven, for example, a continuous infra-red vulcanisation oven of from 5 to about 10m in length and up to 150mm in width, preferably no more than 100 mm in width. The oven can be adapted to operate at any suitable temperature up to about 400°C, but preferably operates between 150 and 300°C.

[0014] Preferably there is only one region along the barrel where the one or more additive introduction means is/are situated. In the case of there being greater than one additive introduction means, they are preferably all situated at the same distance along the barrel from the inlet, i.e. in a ring around the barrel feeding into a single mixing zone section within the extruder barrel.

[0015] In such cases each additive introduction means can be the same or different. Preferably there is one or two additive introduction means, most preferably there is only one additive introduction means.

[0016] The or each additive introduction means may be any suitable apparatus for the purpose of supplying additive into the mixing zone section. Preferred additive introduction means include single or twin screw extruders, gear pumps and/or hydraulic piston driven units, of these single or double screw transportational extruders are most preferred. In the case when an additive introduction means is a single screw transportational extruder, it preferably has a screw diameter which is no greater than that of the single screw extruder in accordance with the present invention. Preferably the ratio of the diameter of the single screw extruder screw to the diameter of a single screw transportational extruder screw is from 3:1 to

1.1, more preferably 1.5:1 to 2.5:1, most preferably about 2:1. Preferably the side arm extruder screw has a diameter which is about half that of the single screw extruder screw, e.g. when the single screw extruder screw is 90mm diameter the side arm extruder screw is 45mm diameter. Henceforth the means of introducing an additive may be described as a "side arm extruder" but it should be understood that when discussed in general terms this is merely for the sake of simplification and may be interpreted to mean any suitable unit for introducing the additive into the single screw extruder in accordance with the present invention.

[0017] Preferably the screw of the single screw extruder in accordance with the present invention has one or more flights which is/are provided to assist in the transport of polymer and/or polymer/additive mixture through the extruder from the inlet to the outlet. Preferably the screw is divided into substantially four sections each section having a different geometry and function from the others. The four sections are a transportational screw section, a mixing zone section a mixing screw geometry section and a compression screw section.

[0018] When the screw of the single screw extruder in accordance with the present invention is situated in the extruder barrel, the transportational screw section is preferably situated between the inlet and the plug and is utilised to transport polymer along the barrel to the plug. It comprises a flight of any appropriate geometry used in the transportation of silicone rubber through a transportational silicone rubber extruder.

[0019] The mixing zone section is situated immediately adjacent to the side of the plug furthest away or downstream of the inlet and as such polymer passing through apertures in the plug immediately enter the mixing zone section when exiting the aperture through which it has passed. The fact that the plug is an obstruction in the way of the polymer travelling along the extruder barrel means that as polymer moves closer to the plug it is under an increasing pressure. However once polymer passes through one of the apertures because there is no further obstruction it enters the mixing zone section at a significantly reduced pressure compared to polymer at the side of the plug nearest the inlet.

[0020] Each side arm extruder has an introduction means for introducing additive into the mixing zone. This may take the form of an injection port for transfer of additive into the single screw extruder, which in effect is an obstruction in the pathway of the additive

travelling along the side arm extruder barrel and as such as the additive moves closer to the plug it is under an increasing pressure. As only small volumes of additive reaching the injection port, at any moment in time, may pass through the injection port a pressure drop also occurs when additive enters the mixing zone and it is believed that it is the effect of this pressure reduction in relation to both the additive and polymer which enhances their inter-mixing in the mixing zone.

[0021] It was found that the actual pressure required in the side arm extruder and in the single screw extruder in accordance with the present invention varied dependent on the additive and polymer used for example in some instances the pressure required in the single screw extruder in accordance with the present invention was significantly lower than in the side arm extruder. In respect to fluid flow it will be appreciated that the mixing is caused by the break up and reorientation of the laminar flow streams of polymer and additive upon entering the mixing zone. In one embodiment it was found that the pressure on the additive in the side arm extruder about to be introduced into the single screw extruder was between approximately 2 to 6 times as great as that of the polymer immediately upstream of the plug. In this embodiment it was most preferred for the pressure on the additive to be four times the pressure of polymer, for example if the pressure in the side arm extruder were 120 bar ( $120 \times 10^5$  Pa) the pressure immediately before passing through the plug would be approximately 30 bar ( $30 \times 10^5$  Pa).

[0022] The mixing zone section is deemed to end where flights used for the mixing screw geometry section begin on the screw downstream of the mixing zone. Polymer/additive mixture issuing from the mixing zone section, although already relatively well mixed, is subsequently subjected to further mixing using the mixing screw geometry section to thoroughly mix the additive into the polymer so that a homogeneous polymer/additive mixture is obtained prior to entering the compression section. The flight(s) of the mixing screw geometry section is/are preferably in the form of a double flight with varying flight pitches, most preferably where one flight has a smaller diameter than the other to enable back flow and thereby promoting additional mixing as the polymer/additive mixture progresses along the extruder barrel towards the outlet.



[0023] The compression screw section is positioned between the mixing screw geometry section and the outlet and is designed to compress the polymer/additive mixture to remove air pockets or the like prior to exit from the barrel typically through an extruder head. Any suitable flight geometry, currently used for compressing in silicone rubber extruder  
5 technology may be utilised.

[0024] Preferably the barrel and screw are both cylindrical and the plug is an integral part of the screw and is shaped such that its outer edges are sized to prevent polymer passing downstream of the plug in any way other than through the apertures in the plug. The  
10 apertures in the plug may be randomly positioned but must provide a means of transferring polymer past the plug and into the mixing zone section. Preferably the apertures are annularly disposed around the periphery of the plug. The apertures may be formed between the inner barrel wall and the outer edge of the plug, for example in the form of teeth. Alternatively the outer edge of the plug is sized such that no polymer may pass between the  
15 outer edge of the plug and the inner barrel wall. In the latter case the plug is an annular flight on the screw body and the apertures are formed in the annular flight such that polymer or a polymer/additive mixture upstream of the plug may pass through the apertures in the plug and into the mixing zone. In a further alternative the apertures may be a combination of the above two options, however the first of the above options is preferred for ease of cleaning and the  
20 decreased likelihood of blockages in the apertures.

[0025] When the apertures in the plug are formed entirely in the body of the plug, each aperture may have any shape but preferably has a circular cross-section with a diameter which is smaller than the width of the annular flight. Preferably there is a plurality of equally  
25 spaced apertures around the annular flight of the plug, these may be of any appropriate shape but preferably have the appearance of teeth projecting outwardly from the plug such that polymer would only be allowed through the plug by passing through gaps formed between adjacent teeth and the inner wall of the single screw extruder barrel. Preferably the cumulative cross-sectional area of the apertures is less than half the surface of one side of the  
30 annular flight of the plug and is more preferably less than 25%. For a 90mm diameter screw apertures in the form of teeth may be sized 3mm deep and 3 mm wide, apertures in the form of a circular cross-section may have a diameter of 5mm or less.

[0026] The additive may be introduced into the barrel of the single screw extruder through a single outlet i.e. directly or may be directed from the end of the side arm extruder into a substantially cylindrical channel formed in or using a casing around the main barrel of the single screw extruder which has a plurality of holes connecting the channel to the mixing zone section such that additive may be introduced into the mixing zone section from a plurality of sites to enhance mixing capabilities between polymer and additive, in either case there being a significant pressure reduction when entering the mixing zone section. Preferably the cylindrical channel is in the form of an annular ring. Preferably the substantially cylindrical channel is arranged around the whole of the barrel but may be alternatively have a C-shaped cross-section such that additive would enter the channel and take one of two arms, each arm having a plurality of sites.

[0027] In one embodiment of the invention the preparation of a constant mixture was obtained by keeping the temperature and pressure in both the single screw extruder upstream of the plug and the side arm extruder constant which in turn lead to constant mixing in the mixing zone section of polymer and additive. It was found that, as might be expected, the required pressures vary particularly with the viscosity of the polymer and additive being used. However, it is relatively straightforward for a man skilled in the art to determine the appropriate relative screw speeds of the single screw extruder in accordance with the present invention and the side arm extruder. It was found that for many cases that the relative screw speeds for the single screw extruder and the side arm extruder may be determined by use of the following equation:-

$$\text{rpm}_{x/2} = \text{rpm}_x \times \frac{\text{weight \% B}}{\text{weight \% A}} \times \frac{V_{r(x/2)}}{V_{r(x)}}$$

wherein  $\text{rpm}_{x/2}$  and  $\text{rpm}_x$  are the speeds (revolutions per minute) of the sidearm extruder screw and single screw extruder screw respectively and  $V_{r(x/2)}$  and  $V_{r(x)}$  are the reduced volumes of the additive and polymer between adjacent screw flights on the side arm extruder screw and single extruder screw respectively. Theoretically the volume of a substance travelling along a screw in an extruder is the actual volume which can be determined by simple mathematics, however it is to be appreciated that extruder systems operate under relatively high pressures which typically result in slippage in the vicinity of the barrel wall, in turn resulting in a

reduction in screw output which reduces as pressure increases and thereby a reduction in apparent "reduced volume" within the extruder increases, the term reduced volume in the above equation relates to such a value.

5    [0028]        In each case  $V_r = V_t \cdot \eta_r$  where  $V_r$  is the reduced volume,  $V_t$  is the theoretical volume and  $\eta_r$  is a dimensionless constant which may be experimentally determined for each extruder.

10    [0029]        It is necessary to ensure that the temperature and pressure relationship between the polymer entering the mixing zone through the plug and additive being introduced by way of the additive introduction means are controlled so that substantially constant predetermined amounts of polymer and additive are mixed at all times in order to obtain the best results for the invention. Any appropriate pressure and temperature monitoring means may be utilised. The barrel temperature of both the single screw extruder in accordance with the present  
15    invention and the side arm extruder may be controlled by an appropriate heating/cooling means.

20    [0030]        Preferably the single screw extruder in accordance with the present invention is utilised for the extrusion of silicone rubber and as such only requires a cooling means which may take the form of a single cooling unit along the whole length of the respective extruder barrel, but preferably is arranged zonally so that a plurality of cooling zones are provided along the barrel using cooling water and controlled by any appropriate means for example by means of a manual ball valve with a flow rate indicator or with a one set-point temperature controller and cooling the barrel with a solenoid valve.

25

30    [0031]        In one preferred embodiment there is provided a control system such that in the event of a pressure drop or temperature change being recorded outside a predetermined range the pressure/temperature control unit may send a signal to adjust the temperature, i.e. to increase the flow rate of cooling water around the appropriate section of the barrel or may vary the rate of introduction of polymer or additive to adjust the ratio back to being within the predetermined range.

[0032] The output of the single screw extruder in accordance with the present invention can be anything up to 500 kg per hour but is preferably in the range of 30 to 200 kg per hour.

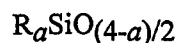
5 [0033] In a most preferred embodiment the polymer is a silicone rubber. The silicone rubber will preferably comprise an organopolysiloxane polymer, optionally filler such as reinforcing silica filler and a curing component.

[0034] In a further embodiment of an invention there is provided a method of  
10 continuously mixing a silicone rubber comprising an organopolysiloxane polymer, optional filler and a curing component with an extruder as hereinbefore described;

Wherein

- 15 i) polymer is transported from the inlet to the plug and through the plug by way of the apertures into a mixing zone and one or more additives is/are introduced into the mixing zone by way of the one or more additive introduction means
- ii) the resulting polymer/additive mixture is further mixed by way of the screw to form a homogenous mixture and
- 20 iii) extruding the homogeneous mixture from the extruder.

[0035] The organopolysiloxane polymer substantially consists of units of the  
25 following average formula:-



wherein, R is selected from substituted and unsubstituted monovalent hydrocarbon groups and is exemplified by alkyl groups such as methyl, ethyl, and propyl; alkenyl groups such as vinyl, allyl, butenyl, and hexenyl; aryl groups such as phenyl; and aralkyls  
30 such as 2-phenylethyl, said substituted groups may be, for example halogen groups preferably fluoro groups and  $a$  is a value of from 1 to 4 but in the majority of units  $a$  will be 1.95 to 2.05.

[0036] The organopolysiloxane polymer preferably has at least 2 silicon-bonded alkenyl groups in each molecule. The alkenyl groups can be bonded in pendant and/or terminal positions. The molecular structure of the organopolysiloxane polymer generally has a degree of polymerization (dp) in the range of from 200 to 20,000, but is preferably greater than about 1500. The organopolysiloxane polymer may be a homopolymer or a copolymer or a mixture of such polymers. The siloxy units in the organopolysiloxane polymer are exemplified by dimethylsiloxy, vinylmethylsiloxy and methylphenylsiloxy units. The molecular terminal groups in the organopolysiloxane polymer are exemplified by trimethylsiloxy and vinyldimethylsiloxy groups.

10

[0037] The organopolysiloxane polymer is exemplified by any of the following:- vinyldimethylsiloxy-endblocked dimethylsiloxane-vinylmethylsiloxane copolymer, vinyldimethylsiloxy-endblocked polydimethylsiloxane, vinylmethylhydroxysiloxy-endblocked dimethylsiloxane-vinylmethylsiloxane copolymer, and vinyldimethylsiloxy-endblocked dimethylsiloxane-methylphenylsiloxane-vinylmethylsiloxane copolymer.

15

[0038] Typically, silicone rubber compositions used in silicone extruders, to make for example wires and cables, usually use polymers with a stiff, gum-like consistency. Generally, these stiff gum-like polymers have a degree of polymerisation of above about 1500 and have a Williams plasticity number (ASTM D926) in the range of from about 30 to 250, and preferably from 95 to 125. The plasticity number, as used herein, is defined as the thickness in millimetres x 100 of a cylindrical test specimen 2 cubic cm in volume and approximately 10 mm in height after the specimen has been subjected to a compressive load of 49 Newtons for three minutes at 25°C. The single screw extruder of the present invention is primarily intended for use with these types of silicone rubber compositions.

20

25

[0039] The composition will also include one or more inorganic fillers suitable for use in combination with silicone rubber compositions. Such inorganic fillers may be represented by a fumed silica or dry-process silica, wet-process silica or sedimentary silica, silica aerogels or a similar reinforcing silica having a specific surface area greater than 50 m<sup>2</sup>/g and preferably 150 to 400 m<sup>2</sup>/g. Other fillers which may be used include a diatomaceous earth powder, calcium carbonate quartz powder, powdered aluminium

30

hydroxide, powdered aluminium oxide, powdered magnesium oxide, titanium dioxide and mica.

[0040] The filler can be used individually or in combination of two or more.

5 Reinforcing fillers are preferred as they provide increased mechanical properties in heat cured silicone rubber compositions. In the case of a reinforcing filler, it is preferred to treat the reinforcing silica filler to render its surface hydrophobic, as typically practiced in the silicone rubber art. This can be accomplished by reacting the reinforcing silica filler with a liquid organosilicon compound which contains silanol groups or hydrolysable precursors of silanol  
10 groups. Compounds that can be used as filler treating agents, also referred to as anti-creeping agents or plasticisers in the silicone rubber art, include such ingredients as low molecular weight liquid hydroxy- or alkoxy-terminated polydiorganosiloxanes, including  $\alpha,\omega$ -silanediols, hexaorganodisiloxanes, cyclodimethylsiloxanes and hexaorganodisilazanes such as hexamethyldisilazane and dimethyldichlorosilane or, trimethylchlorosilane. The filler is  
15 typically added at a level of from about 1 to 65 weight percent of the weight of the total composition, and preferably in a range of 5 to 25 weight percent of the total composition.

[0041] The curing component can be any of the well-known curing components known in the silicone rubber art. For example, the curable silicone rubber compositions  
20 suitable for use with this invention may be cured to an elastomeric state by exposure to electron beams, ultraviolet rays, electromagnetic waves, or heat. Where heat is used as the curing mechanism, an organic peroxide curing catalyst may be used. Examples of suitable organic peroxide curing catalysts include 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, 2,2-bis(t-butylperoxy)-p-diisopropylbenzene, 1,1-bis(t-butylperoxy)-  
25 3,3,5-trimethylcyclohexane, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexyne-3, di-t-butylperoxide, benzoyl peroxide, p-chlorobenzoyl peroxide, dicumyl peroxide, tertiary butyl peracetate, tertiary butyl perbenzoate, monochlorobenzoyl peroxide, 2,4-dichlorobenzoyl peroxide, and tertiary butyl cumyl peroxide. The amount of catalyst used will depend on the type of catalyst and may be determined by experimentation.  
30 Generally, organic peroxide catalysts are useful in amount of from about 0.05 to 10 parts, and more preferably 0.1 to 5 parts by weight catalyst per 100 parts by weight of the organopolysiloxane polymer.

[0042] When using an organic peroxide catalyst the maximum temperature permissible in the main barrel is 80°C. A temperature greater than 80°C causes serious problems with respect to viscosity control in that it will be impossible to control the viscosity which will decrease with increase in temperature resulting in lower pressure in the extruder which in turn results in both poorer mixing and fluctuation in flow along the extruder barrel. Most preferably the temperature should always be less than 50°C for organic peroxide cure systems.

[0043] An alternative curing component which is applicable is an organohydrogensiloxane crosslinker used in the presence of a platinum group metal-containing catalyst. The organohydrogensiloxane crosslinker must contain an average of at least two silicon-bonded hydrogen atoms per molecule, and no more than one silicon-bonded hydrogen atom per silicon atom, the remaining valences of the silicon atoms being satisfied by divalent oxygen atoms or by monovalent hydrocarbon radicals comprising one to seven carbon atoms. The monovalent hydrocarbon radicals can be, for example, alkyl groups such as methyl, ethyl, propyl, tertiary butyl, and hexyl; cycloalkyl groups such as cyclohexyl; and aryl groups such as phenyl and tolyl. Such materials are well known in the art. The molecular structure of the organohydrogensiloxane may be linear, linear with a degree of branching, cyclic, or of a network-form. There are no particular restrictions on the molecular weight of the organohydrogensiloxane, however it is preferable that the viscosity at 25°C is between 3 to 10,000 mPa.s. Furthermore, the organohydrogensiloxane is added in an amount such that the ratio of the number of moles of silicon-bonded hydrogen atoms to the number of moles of silicon-bonded alkenyl groups is in the range of from 0.5:1 to 20:1, and preferably in the range of from 1:1 to 5:1. If the molar ratio is less than 0.5:1, curing of the present composition becomes insufficient, while if the molar ratio exceeds 20:1, hydrogen gas is evolved resulting in foaming during the curing process.

[0044] Any suitable platinum group metal-containing catalyst which is known to catalyse the reaction of silicon-bonded hydrogen atoms with silicon-bonded vinyl groups may be used. By platinum group metal, it is meant ruthenium, rhodium, palladium, osmium, iridium, and platinum. Platinum based catalysts are particularly preferred. Examples of such platinum based catalysts include chloroplatinic acid, alcohol solutions of

chloroplatinic acid, complexes of chloroplatinic acid with olefins, complexes of chloroplatinic acid with divinylsiloxane, platinum black, metallic platinum, and catalysts in which metallic platinum is supported on a support. The amount of catalyst added varies according to the type of catalyst used, and is not especially restricted; ordinarily, however, 5 the amount added is between from 1 to 1,000 parts by weight, preferably 5 to 100 parts by weight of platinum group metal, per 1,000,000 parts by weight of polymer. It should be noted that when using the platinum curing system temperatures in the single screw extruder of 35°C or above may result in the partial curing or scorching of the polymer and/or polymer/additive mixture in the single screw extruder. Preferably the system will be cooled 10 by a cold water wrap around the length of each barrel with the water being utilized to keep the temperatures below 8°C is particularly preferred when using the platinum cure system.

[0045] When using platinum curing technology there may be provided one or two additive introduction means. When one is utilized it will contain the required cross-linker 15 and if/where necessary pigment or other additive. When two additive introduction means are provided one may contain the cross-linker and the other the pigment. In the latter case the additive introduction means are preferably both extruders or one is an extruder and the other may comprise a pumping unit.

20 [0046] When the organopolysiloxane polymer is a vinyl dimethylsiloxane-containing gum, it is preferred that the curing component be selected from the organic peroxide curing agents. When the organopolysiloxane polymer is a vinyl dimethylsiloxane-containing liquid with viscosity of less than 150,000 mPa.s, it is preferred that the curing component comprises an organohydrogensiloxane crosslinker and a platinum group metal- 25 containing catalyst.

[0047] Optional additional additives include smoke reducing agents selected from materials frequently used in the silicone rubber industry to reduce smoke, including platinum, aluminium trihydrate and magnesium oxide. Other optional ingredients may 30 include tensile modifiers, heat stabilizers, lubricants and wollastonite (calcium metasilicate).



[0048] In a most preferred embodiment polymer introduced into the main inlet is a naturally coloured silicone rubber compound comprising polymer filler and curing component and the additive in the side arm extruder(s) is a colouring additive for colouring the aforesaid silicone rubber compound whilst in the extruder and/or in the case of the use of a platinum cure system the additive may include the cross-linker.

[0049] Any appropriate silicone rubber compound may be utilised for the polymer for example for an organic peroxide cure system the polymer may consist of 100 parts by weight of organopolysiloxane polymer, 50 parts by weight of a filler 1.7 parts by weight of organic peroxide catalyst such as 2,4-dichlorobenzoylperoxide and 0.5 parts by weight of a viscosity modifier, other typically used ingredients in the silicone rubber compound may be flame retardant additives and heat resistance additives dependent on the end use of the product. The pigment additive is preferably in the form of a masterbatch comprising, for example, be a mixture of 100 parts by weight of organopolysiloxane polymer and up to 100 parts by weight of pigment. A greater proportion of pigment in such a mixture would increase the viscosity of the resulting additive to an amount which would be too high for the additive to be mixed into the colourless silicone rubber base.

[0050] In the case of a platinum cure system the compositions may for example comprise 100 parts by weight of organopolysiloxane polymer with 20 parts by weight of filler 0.8 parts by weight of platinum catalyst and 0.8 parts by weight of a catalyst inhibitor and where a single side arm extruder is used the additive might comprise 100 parts by weight of organopolysiloxane polymer, 30 parts by weight of cross-linker and 30 parts by weight of colour pigment.

[0051] Advantages for introducing colour pigment by a method in accordance with the present invention include, for example, the fact that for the wire cable coating market innumerable coloured cables may be required, this currently means that a wire coating operation needs to maintain a very high stock requiring silicone rubber of each colour hence high storage costs and a need for excellent stock control. However, by supplying natural coloured silicone rubber together with a variety of pigment additives for the side arm extruder, stock control is significantly more manageable and space required for stock would be reduced as the user would only need to maintain stocks of comparatively small volumes of

pigment as opposed to high volumes of differently coloured rubbers. This also reduces costs for the silicone rubber manufacturer who does not need effect the colouring of the products in house and can supply natural product direct to the customer. It is estimated that processing costs could be reduced by as much as 15% annually while at the same time yielding an  
5 excellently mixed consistent silicone rubber product.

[0052] Further advantages can be seen when using an extruder system of the present invention when the polymer is cured using a platinum catalyst, there should be no shelf life limitations, faster extrusion rates and the ability to vary the amounts of some components  
10 dependent on the use, curing requirements (as compared to a one part platinum catalysed system where all components are supplied in a single composition by the supplier). In the case of the platinum cure system one further added advantage is the elimination of the need for post-cure treatment for non-food applications as the resulting silicone rubber product has an improved final cure. This invention allows for easy variation of cure speed.

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[0053] Other uses include extrusion of fluorosilicones and in the making of silicone rubber sponges.

[0054] It should be understood that the side arm extruder and screw can be adapted to  
20 fit pre-existing extruders and as such can be provided in the form of a kit.

[0055] A specific embodiment of the invention will now be provided with the aid of the following drawings in which

25

- Fig.1 is an overall view of the system

- Fig.2 shows the screw of the single screw extruder and Fig.2a is an expansion of a section of the mixing geometry zone

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- Figs.3a and 3b show cross-sectional views of the plug through the points I-I on Fig. 2.
- Fig.4 is a view of the inlet from side arm extruder into the single screw extruder

- Fig. 5 is provided to explain how to determine the relative screw speeds of the different extruders in one embodiment of the invention.

[0056] In Figure 1 there is provided a single screw extruder 1 and a side arm extruder

5 2. Single screw extruder 1 has a cooling system 3 surrounding the barrel 100 which has an inner wall 102 and an extruder head attached 4 for shaping the resulting product prior to curing in an appropriate curing oven (not shown), an outlet 5, a screw 6 (which is described in detail in Fig.2) an inlet 7 and a plug 12. Side arm extruder 2 has a screw 8 a cooling system 9 and an outlet 10 into the single screw extruder 1. Outlet 10 is in direct contact with channel  
10 200 having a plurality of entry holes 202, which in use, enable additive from side arm extruder 2 to be introduced into single screw extruder 1 at a plurality of positions (described in detail in Fig. 4).

[0057] In Figure 2 there is provided a detailed drawing of the single screw extruder

15 screw 6 of the present invention in which there is a screw body 104, a transportational screw section A, a mixing zone section B, a mixing screw geometry section C and a compression screw section D. The flight 11 of transportational screw section A is designed to transport polymer loaded in the feed area to plug 12 which separates transportational screw section A from mixing zone section B. Mixing zone section B is positioned to be in line with outlet 10  
20 from the side arm extruder. The diameter of the body 104 of the screw 6 may be smaller than for the rest of the body in order to provide an increased volume in the mixing zone B. Mixing screw geometry section C has double flights 14 and 16 which are of variable pitch to effect mixing. As will be seen from Fig 2a flight 16 is sized so that there is space between the periphery of the flight and inner wall 102 of barrel 100 (Fig. 1) in order to permit back flow  
25 but flight 14 is sized to prevent backflow of polymer. Compression screw section D comprises flight 17 on body 104.

[0058] Fig. 3a is a cross-sectional view of the plug 12 showing in dotted lines the outline of the circumference of screw body 104, the annular flight forming the stopper 18 and  
30 a series of apertures 20 adapted to interconnect transportational screw section A and mixing zone section B.

[0059] Fig.3B is a cross-sectional view of an alternative plug in which instead of the apertures 20 being formed in the body of the plug as in Fig.3a, they are formed around the outer periphery of the plug such that in use polymer upstream of the plug will move downstream of the plug through apertures 20a formed between the outer periphery of the plug and inner wall 102 of barrel 100.

[0060] Fig. 4 shows one way in which additive is introduced into single screw extruder 1 from side arm extruder 2 via outlet 10. Additive is transported along the side arm extruder 2 and out through the outlet into annular channel 200. Annular channel 200 is connected to the single screw extruder through holes 202.

[0061] Hence, in use, polymer is introduced onto the single screw extruder 1 via inlet 7, polymer is then transported through transportation screw section A as far as plug 12, with pressure on the polymer increasing to a maximum when reaching plug 12. The only way for polymer to move downstream of the plug is by travelling through apertures 20 or 20a and as such as soon as polymer enters the mixing zone B from the apertures it is immediately subjected to a significant pressure reduction.

[0062] Additive is transported through the side arm extruder and is introduced into mixing zone B through outlet 10 at a significantly greater pressure than polymer which has passed through apertures 20 or 20a, thereby causing partial mixing of the polymer and additive in mixing zone B. Temperature and pressure sensors (not shown) are utilised in the single screw extruder and the side arm extruder to ensure that the respective temperature and pressure at which polymer and additive enters mixing zone B is maintained substantially constant throughout the duration of an extrusion run.

[0063] The partially mixed polymer and additive is then transported into mixing screw geometry section C and is subjected to further mixing due to the sizing and pitch of flights 14 and 16. Homogeneously mixed polymer and additive is then transferred into compression screw section D wherein flight 17 is adapted to compress the homogeneous mixture to remove air pockets or the like prior to passing through outlet 5 and into extruder head 4. It should be noted that when the additive is introduced into the mixing zone section B from multiple holes as described with the help of Fig.4 additive is transported along the side

arm extruder 2 and out through outlet 10 into annular channel 200. The additive is then forced out of annular channel 200 through holes 202 and thereby introduces additive into the mixing zone section B of the single screw extruder through a number of sites simultaneously which enhances the mixing of polymer and additive in the mixing zone section.

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[0064] Fig.5 is intended to show how the relative screw speeds of the single screw extruder and the side arm extruder are determined. It will be noted that in this case an alternative outlet 10 is depicted whereby additive is introduced directly from outlet 10 through a single aperture 204 into mixing zone B. For the example provided below the screw diameter of single screw extruder 1 was 90mm and that of the side arm extruder was 45 mm. The pressure on additive in the side arm extruder was maintained at substantially 120 bar ( $120 \times 10^5$  Pa) and was periodically checked. The pressure of polymer immediately upstream of plug 12 of the single screw extruder was maintained at substantially 30 bar ( $30 \times 10^5$  Pa) and was periodically checked. Values of the reduced volume ( $\text{dm}^3/\text{rpm}$ ) were determined from the values of the theoretical volume and  $\eta_{tr}$  in Table 1 below. The speed of the single screw extruder screw was set at 5 rpm and in the examples shown as examples 1 and 2 the end product consisted of 70% by weight of polymer (A) and 30% by weight of additive. From the above information the required screw speed for the side arm extruder screw was calculated to be approximately 19 rpm on the basis of the following equation, which speed was the utilised for both example 1 and 2. The values utilised are provided in Table 1

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15

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$$\text{rpm}_{45} = \text{rpm}_{90} \times \frac{\text{weight \% B}}{\text{weight \% A}} \times \frac{V_{r(45)}}{V_{r(90)}}$$

25

Table 1

	Single screw extruder (90mm diameter)	Side Extruder (45mm diameter)
$V_t$ ( $\text{dm}^3/\text{rpm}$ )	0.473	0.018
$\eta_{tr}$	0.1 (30 bar, 15d)	0.3 (120bar, 15d)
$V_r$ ( $\text{dm}^3/\text{rpm}$ )	0.048	0.0054
Screw speed	5.0	19.05 (by calculation)

[0065] A number of test runs have been undertaken utilising the above equation in each example the following polymer and additive compositions were used. The test for homogeneous mixing was visual as it was found that poor mixing (as seen with comparative test C1) was clearly observed without the need for additional analysis because the additive was substantially a coloured pigment and poor mixing resulted in colour variations within the resulting products.

[0066] In order to show that cured coloured rubber samples were homogenously mixed a series of physical tests were undertaken for samples mixed in accordance with the extruder of the present invention and these results were compared with rubber mixed on a mill in lab conditions (need conditions). It is to be understood that poor mixing results in poor physical properties of the resulting cured rubber products

#### Example 1

Polymer composition in single screw extruder

[0067] 100 parts by weight of a substantially 1:1 mixture of dimethylvinyl siloxy terminated, dimethyl methylvinyl siloxane and dimethylvinylsiloxy terminated dimethylsiloxane containing 34 weight % of amorphous silica (specific gravity  $1.2\text{g/cm}^3$  and Shore A hardness 70 to 73) and 1.5 parts by weight of 2,4-dichlorobenzoyl peroxide.

[0068] The additive comprised a 50 parts by weight of a dimethylvinylsiloxy terminated dimethyl methyl vinyl siloxane containing 32% by weight of amorphous silica (specific gravity  $1.2\text{g/cm}^3$  and Shore A hardness 71), 50 parts by weight of a blue pigment and 1 part by weight of a handling additive. The mixture was mixed in the extruder in accordance with the present invention and cured in a curing oven. In comparison a similar sample was mixed on a mill at room temperature and pressure for a period of about 3 minutes and the resulting mixture was then pressed in a press mould for 10 minutes at  $170^\circ\text{C}$  and then 5 minutes at  $116^\circ\text{C}$ . Standard physical testing was carried out and it was found that the sample mixed in accordance with the present invention had substantially identical properties as those of the product milled in the laboratory and the results are provided in Table 2.

Table 2: Physical Properties

Physical Properties	Example	Lab prepared sample
Hardness (Shore A)	71	70
Specific Gravity ( $\text{g/cm}^3$ )	1.2	1.2
Modulus 100%	2.5	2.6
Tensile Strength (MPa)	11.7	11.5
Elongation (%)	440	450

**Example 2**

5

Polymer composition in single screw extruder

[0069] 100 parts by weight of a substantially 1:1 mixture of dimethylvinyl siloxy terminated, dimethyl methylvinyl siloxane and dimethylvinylsiloxy terminated dimethylsiloxane containing 34 weight % of amorphous silica (specific gravity  $1.2\text{g/cm}^3$  and Shore A hardness 70 to 73); and 0.8 parts by weight of an ethynyl cyclohexanol inhibitor and 2 parts by weight of platinum catalyst.

[0070] The additive comprised 100 parts by weight of a substantially 1:1 mixture of dimethylvinyl siloxy terminated, dimethyl methylvinyl siloxane and dimethylvinylsiloxy terminated dimethylsiloxane containing 34 weight % of amorphous silica (specific gravity  $1.2\text{g/cm}^3$  and Shore A hardness 70 to 73) 33 parts by weight of a dimethyl methylhydrogen siloxane crosslinker and 5.6 parts by weight of the blue pigment.

[0071] The exact same process as described in Example 1 was utilised and the milling was all done at room temperature. It is to be noted however in example 2 that cross-linker was utilised in the additive and the catalyst used was of the platinum variety. Again the results gave excellent results when compared with the milled product indicating an excellent homogeneous mixing having been achieved as shown in Table 3 below.

25

Table 3

Physical Properties	Example	Lab prepared sample
Hardness (Shore A)	71	70
Specific Gravity g/cm <sup>3</sup>	1.2	1.2
Modulus 100%	2.5	2.6
Tensile Strength (MPa)	11.7	11.5
Elongation (%)	650	660
Tear Strength kN/m	35	35



CLAIMS

- 1) A single screw extruder (1) comprising
  - a) an elongate barrel (100) having an inlet (7) for introducing a polymer into the extruder and an outlet (5) for discharging extruded polymer from the barrel (100)
  - b) a rotatable screw (6) axially disposed within the barrel (100) for advancing polymer in the extruder from the inlet (7) to the outlet (5)
  - c) one or more additive introduction means (2) for introducing at least one additive at one or more predefined positions along the barrel (100) of the single screw extruder (1) between the inlet (7) and the outlet (5),

wherein

immediately upstream of the or each additive introduction means (2) there is provided, on or around the screw (6), a plug (12) having a plurality of apertures (20,20a), said plug (12) being adapted such that, in use, the only way for polymer or polymer/additive mixture to move downstream of the plug (12) is by passing through the apertures (20,20a) and that, having passed through the apertures (20,20a), the polymer or polymer/additive mixture is subjected to a reduction in pressure and is simultaneously mixed with an additive from the one or more additive introduction means (2), prior to transportation of the resulting polymer additive mixture to the outlet (5).

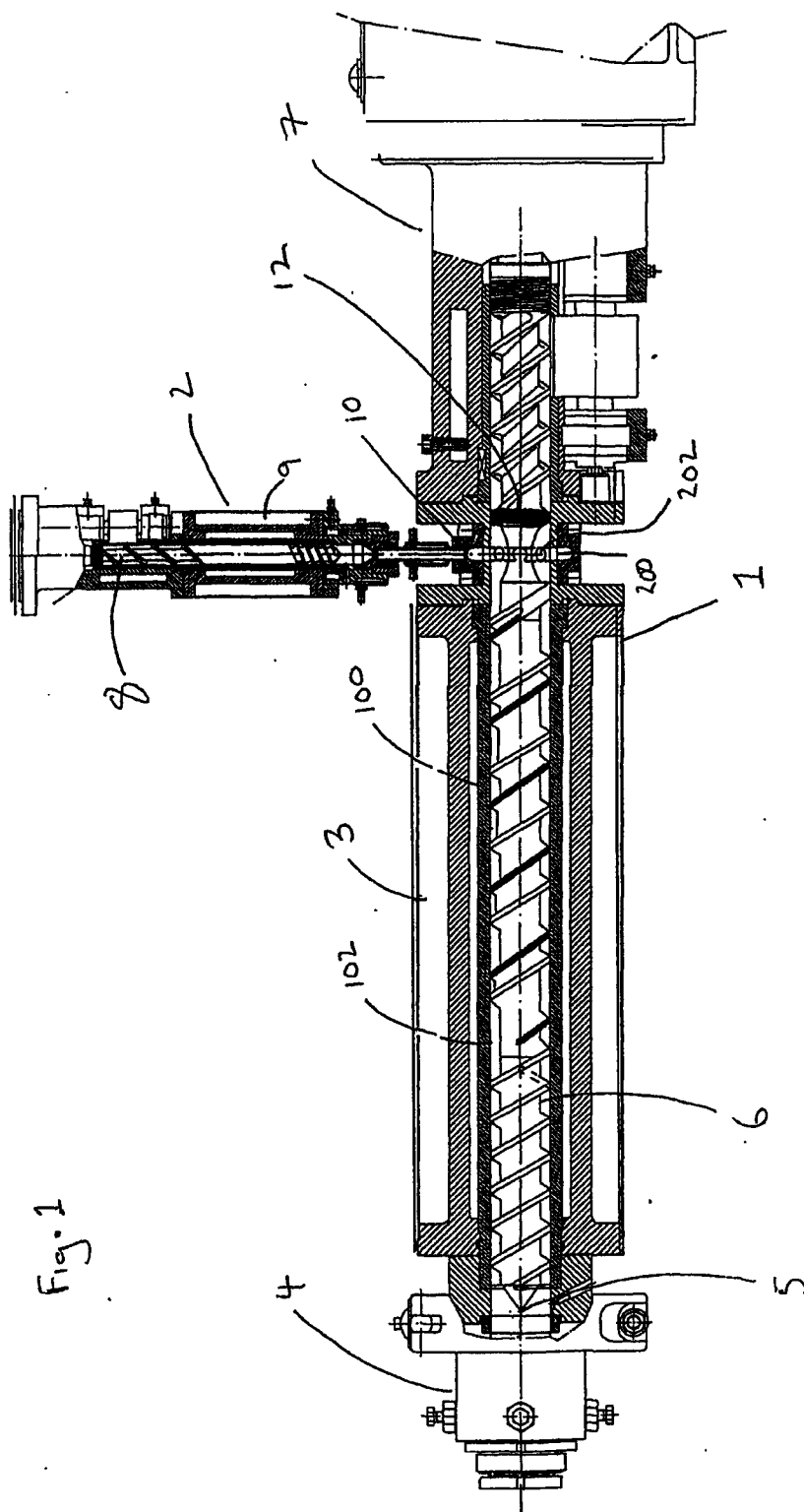
- 2) A single screw extruder in accordance with claim 1 wherein the extruder (1) is a silicone rubber extruder.
- 3) A single screw extruder in accordance with claim 1 or 2 wherein single screw extruder screw (6) is divided into substantially four sections, a transportational screw section (A), a mixing zone section (B), a mixing screw geometry section (C) and a compression screw section (D).

- 4) A single screw extruder in accordance with any preceding claim wherein there is one or two additive introduction means (2).
- 5) A single screw extruder in accordance with any preceding claim wherein each additive introduction means (2) is an extruder.
- 6) A single screw extruder in accordance with any preceding claim, wherein each additive introduction means (2) is connected to the barrel (100) of the single screw extruder (1) through a single outlet (10,204).
- 7) A single screw extruder in accordance with any one of claims 1 to 6, wherein each additive introduction means (2) is connected to a channel (200) formed in or using a casing around the barrel (100) of the single screw extruder (1), said channel (200) having a plurality of apertures (202) such that additive may be introduced simultaneously into the mixing zone section (B) through a plurality of apertures (202).
- 8) A single screw extruder in accordance with any preceding claim wherein the apertures (20a) in the or each plug (12) are teeth situated around the periphery of the plug.
- 9) A single screw extruder in accordance with any one of claims 1 to 8 wherein the plug is an annular flight (18) having a series of apertures (20) in the flight adapted to allow the transfer of polymer or polymer/additive mixture through the apertures (20) into a mixing zone (B).
- 10) A method of continuously mixing a silicone rubber comprising an organopolysiloxane polymer, optional filler and a curing component with an extruder in accordance with any one of claims 1 to 9

wherein

- i) polymer is transported from the inlet (7) to the plug (12) and through the plug (12) by way of the apertures (20,20a) into a mixing zone (B) and one or more additives is/are introduced into the mixing zone (B) by way of the one or more additive introduction means (2)
  - ii) the resulting polymer/additive mixture is further mixed by way of the screw (6) to form a homogenous mixture and
  - iii) extruding the homogeneous mixture from the extruder.
- 11) A method in accordance with claim 10 wherein the additive comprises one or more of a colour pigment, a blowing agent and/or a cross-linking agent.
- 12) A method in accordance with claim 10 or 11 wherein the organopolysiloxane polymer comprises one or more of vinyl dimethylsiloxyl-terminated dimethylsiloxane-vinylmethylsiloxane copolymer, vinyl dimethylsiloxyl-terminated polydimethylsiloxane, vinylmethylhydroxysiloxyl-terminated dimethylsiloxane-vinylmethylsiloxane copolymer, and vinyl dimethylsiloxyl-terminated dimethylsiloxane-methylphenylsiloxane-vinylmethylsiloxane copolymer.
- 13) A method in accordance with any one of claims 10 to 12 wherein the catalyst is an organic peroxide.
- 14) A method in accordance with any of claims 10 to 12 wherein the catalyst is selected from one or more of a chloroplatinic acid, alcohol solutions of a chloroplatinic acid, complexes of a chloroplatinic acid with olefins, complexes of a chloroplatinic acid with divinylsiloxane, platinum black, metallic platinum, and catalysts in which metallic platinum is supported on a support.
- 15) A method in accordance with any one of claims 10 to 14 wherein the pressure on the additive in the additive introduction means (2) about to be introduced into the single screw extruder (1) is from about 2 to 6 times as great as that of the polymer immediately upstream of the plug (12).

- 16) Use of an extruder (1) in accordance with any one of claims 1 to 9 for colouring silicone rubber.
- 17) Use of an extruder in accordance with any one of claims 1 to 9 for introducing a cross-linker into a silicone rubber having a platinum group metal containing cure system.



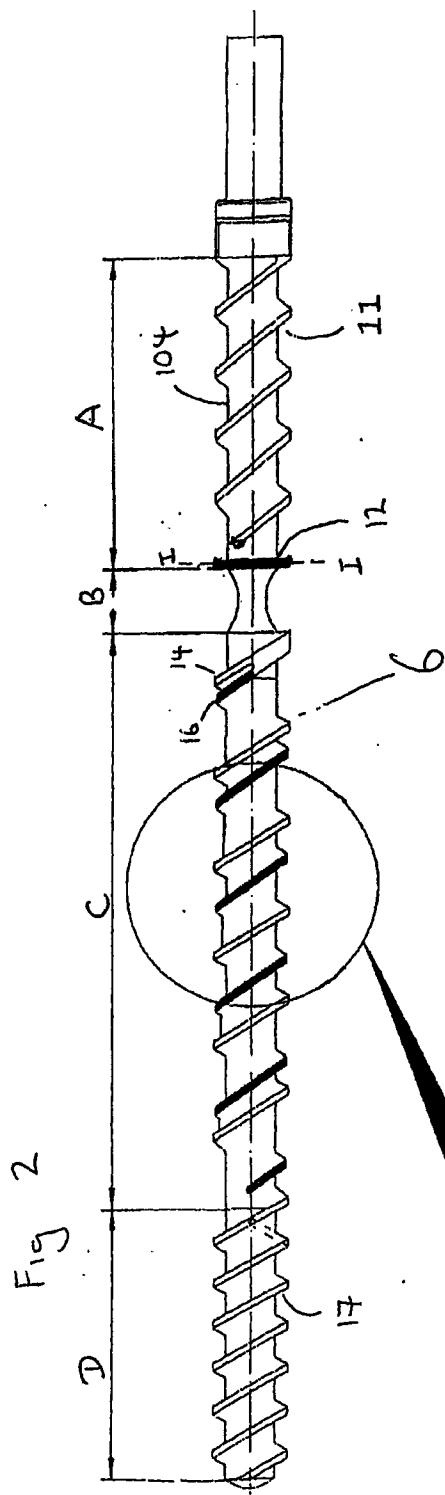


Fig 2a

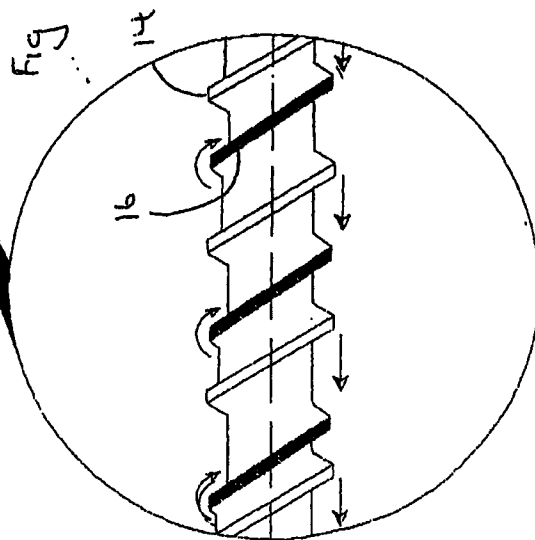
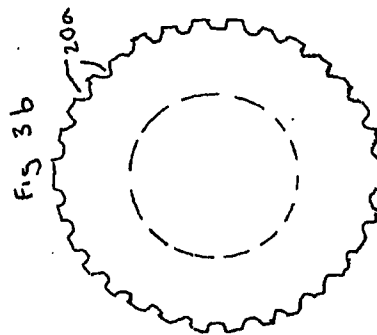
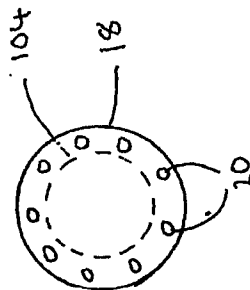
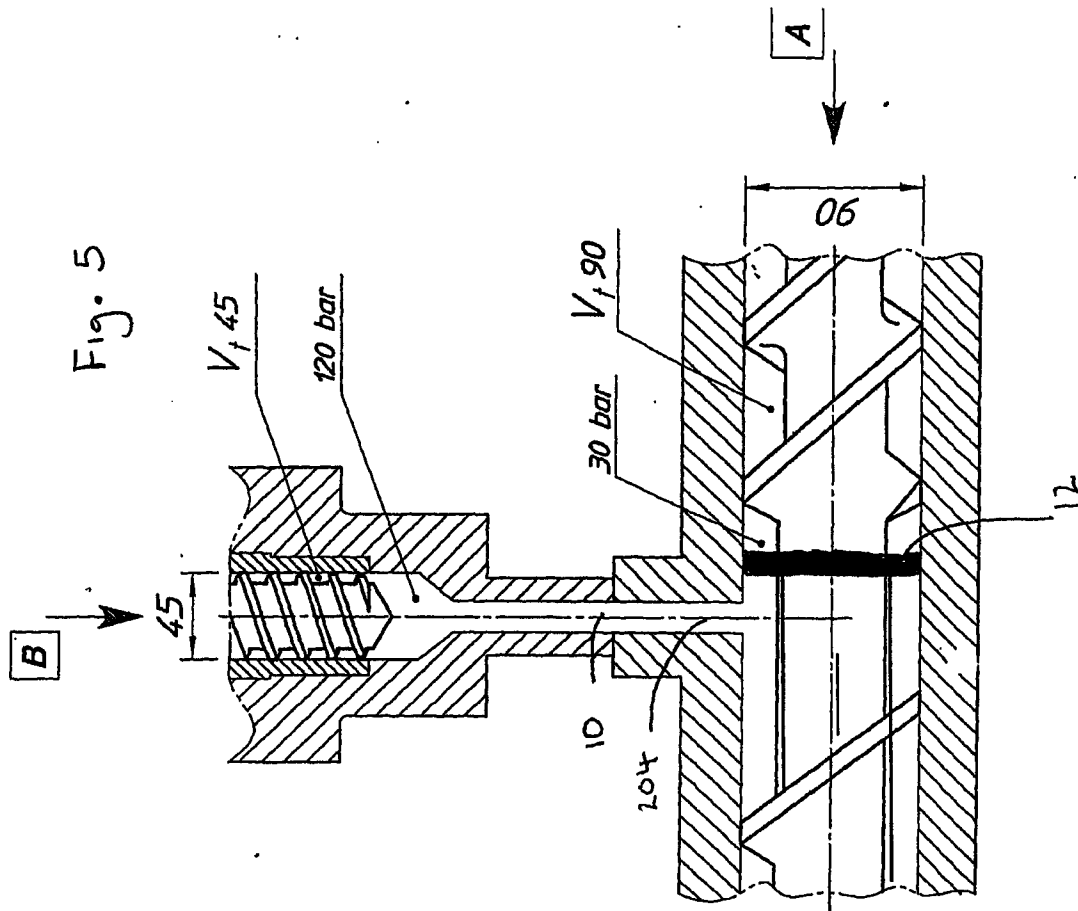


Fig. 3a









## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/10187

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B29C47/10 B29C47/38 //B29K83:00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B29C C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Van Nieuwenhuize, O

## INTERNATIONAL SEARCH REPORT

Internat. Application No.

PCT/EP 02/10187

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